TIRE REINFORCING MEMBER
AND REINFORCED PNEUMATIC TIRE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a tire reinforcing member and a pneumatic tire reinforced with it, particularly to a tire reinforcing member comprising a composite layer comprising a coating rubber layer embedded with steel cords, or a laminate member comprising the composite layer and a rubber composition layer, such as a squeegee rubber, laminated on the composite layer, and a pneumatic tire having its endurance improved by the tire reinforcing member.

2. Description of the Prior Art

Generally, a pneumatic tire is reinforced with steel cords by constructing, for example, a carcass layer comprising at least one ply, a belt layer comprising at least one ply, or a breaker layer comprising at least one ply made from a rubber composition–steel cord composite member. Also conventionally employed is a so-called squeegee rubber to enhance the fatigue endurance of the cord containing layer by laminating one between the layers or plies, thereby improving the endurance of a pneumatic tire.

Since the adhesion failure between the coating rubber composition and the steel cords in the steel cord–coating rubber composite member because of heat build-up during tire operation causes a fatal tire failure, it has been demanded to further enhance the rubber-to-steel cord adhesion. To meet the demand, the coating rubber composition has been generally compounded with a cobalt salt of organic acid as an adhesion promoter to enhance the adhesion to steel cords.

The coating rubber is surrounded by rubber members of various chemical compositions. During a long-term tire operation, various additive components

in the surrounding rubber members migrate into the coating rubber. Some of the migrated components seem to adversely affect the rubber-to-steel cord adhesion. However, this problem has not been sufficiently considered in the prior art.

Japanese Patent Application Laid-Open No. 2000-17115 assigned to the same assignee of this application proposes to deactivate the metal salt of organic acid by compounding a specific water-resistant acid acceptor with a coating rubber which is embedded with steel cords, thereby enhancing the endurance of the rubber-to-steel cord adhesion. However, it turned out that the acid acceptor, when used in larger amounts, also captured sulfur and a vulcanization promoter in the coating rubber composition during the vulcanization, thereby failing to sufficiently improve both the initial adhesion and the resistance to adhesion loss.

SUMMARY OF THE INVENTION

An object of the present invention, in view of the above problems in the prior art, is to provide a tire reinforcing member capable of greatly improving the endurance of a pneumatic tire by dramatically enhancing the resistance to loss of the steel cord-to-coating rubber adhesion without affecting the initial adhesion, and to provide a pneumatic tire having its endurance improved by the tire reinforcing member.

As a result of extensive study, the inventor has found that the above object is achieved by compounding a basic inorganic filler with a rubber composition constituting a coating rubber composition of a composite layer, or a rubber composition layer adjoining to the composite layer to constitute a laminate member comprising the composite layer and a rubber composition layer. The present invention has been accomplished based on this finding.

Thus, the present invention provides a tire reinforcing member comprising at least one composite layer comprising a rubber composition and steel cords, in which a basic inorganic filler is compounded into the rubber

composition.

In the alternative, the tire reinforcing member of the present invention is a laminate member comprising:

(a) at least one composite layer comprising a coating rubber composition and steel cords; and

(b) at least one rubber composition layer comprising a rubber composition, which adjoins to the composite layer;

a basic inorganic filler being compounded into at least one rubber composition constituting the laminate member.

The present invention further provides a pneumatic tire reinforced with the tire reinforcing member mentioned above.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1a is a cross sectional view of an embodiment of the tire reinforcing laminate member of the present invention;

Fig. 1b is a cross sectional view of another embodiment of the tire reinforcing laminate member of the present invention; and

Fig. 1c is a cross sectional view of still another embodiment of the tire reinforcing laminate member of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In a first embodiment, the tire reinforcing member of the present invention comprises at least one composite layer comprising a coating rubber composition and steel cords, in which a basic inorganic filler is compounded into the coating rubber composition constituting a coating rubber.

In the second embodiment, the tire reinforcing member of the present invention is a laminate member comprising:

(a) at least one composite layer comprising a coating rubber composition and steel cords; and

(b) at least one rubber composition layer comprising a rubber composition,

which adjoins to the composite layer,

a basic inorganic filler being compounded into at least one rubber composition constituting the laminate layer.

The tire reinforcing member of the invention is preferably applied to a truck/bus tire or a large-sized off-road tire. The tire reinforcing member is preferably used for constructing at least one ply of any of the carcass layer, a belt layer or a breaker layer of the tire.

The tire reinforcing laminate member may include only one composite layer, or may include two or more composite layers, which are disposed continuously or separately per every rubber composite layer. Basic structures of the tire reinforcing laminate member of the present invention are shown in Figs. 1a to 1c. In the laminate member of Fig. 1a, a rubber composition layer 3 is disposed on one of the outer surfaces of a composite layer 4 comprising steel cords 1 and a coating rubber composition 2. Alternatively, as shown in Fig. 1b, the laminate member may be constructed by the rubber composition layer 3 disposed on one of the outer surfaces of a laminate comprising two composite layers 4 which are continuously laminated one on the other. Also, a rubber composition layer 3 may be interposed between two adjacent composite layers 4 as shown in Fig. 1c. Two or more of any of these laminate members may further be laminated.

In the present invention, at least one of the outer most layers of the tire reinforcing laminate member is preferably a rubber composition layer 3.

The thickness of each layer of the reinforcing member is not particularly limited and selected according to the size and type of the tire to which the member is applied, and can be the same as or different from each other.

It is critical in the present invention to incorporate a basic inorganic filler into at least one of the rubber composition, which constitutes the tire reinforcing member.

The basic inorganic filler may include a metal oxide such as MgO, CaO, and Al_2O_3; a metal carbonate such as $MgCO_3$ and $CaCO_3$; and a basic

composite salt such as talc, kaolin, and hydrotalcite mineral. Of the above basic inorganic fillers, preferred are a hydrotalcite mineral represented by the following Formula I and its calcined product:

$$[(M_1^{2+})_{(1-x)}(M_2^{3+})_x(OH^-)_2]^{x+}\cdot[(A^{n-})_{x/n}\cdot mH_2O]^{x-} \qquad (I)$$

wherein M_1^{2+} is a divalent metal cation, M_2^{3+} is a trivalent metal cation, A^{n-} is an n-valent anion, x is a number satisfying $0 < x \leq 0.5$, and m is zero or a positive number.

More specifically, M_1^{2+} is a divalent metal cation such as Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, and Mg^{2+} is particularly preferable. M_2^{3+} is a trivalent metal cation such as Al^{3+}, Fe^{3+}, Cr^{3+}, Co^{3+}, and In^{3+}. A^{n-} is an n-valent anion such as OH^-, F^-, Cl^-, Br^-, NO_3^-, CO_3^{2-}, SO_4^{2-}, $Fe(CN)_6^{3-}$, CH_3COO^-, oxalate ion, and salicylate ion, and CO_3^{2-} is particularly preferable.

The hydrotalcite mineral, for example, $Mg_{4.3}Al_2(OH)_{12.6}CO_3\cdot m'H_2O$ (x is 0.315 in the Formula I) and its calcined product having the crystal water removed are commercially available from Kyowa Chemical Industry, Co., Ltd.

The compounding amount of the basic filler is not particularly limited and can be chosen according to the use.

When the basic inorganic filler is compounded into the rubber composition constituting the rubber composition layer adjoining to the composite layer, preferable compounding amount is from 0.1 to 20 parts by weight based on 100 parts by weight of the rubber component of the rubber composition. When the amount is less than 0.1 parts by weight, sufficient improvement may not be obtained on the resistance to adhesion loss caused by, for example, heat generated during the tire operation. An amount exceeding 20 parts by weight is likely to reduce the fracture resistance, fatigue resistance of the vulcanized rubber composition and workability of the unvulcanized rubber composition. More preferred amount of the basic inorganic filler is 0.5 to 10 parts by weight in view of the resistance to adhesion loss, fatigue resistance of the vulcanized rubber composition, and workability of the unvulcanized rubber composition.

On the other hand, when the basic inorganic filler is compounded into the coating rubber composition of the composite layer of the tire reinforcing member, the amount of the basic inorganic filler to be compounded is preferably 0.1 to 5 parts, more preferably 0.1 to 2 parts, by weight based on 100 parts by weight of the rubber component of the coating rubber composition in view of enhancing the endurance of the tire.

The rubber component for the rubber composition of the tire reinforcing member may be natural rubber and/or synthetic rubber. The synthetic rubber usable in the present invention is, for example, butadiene rubber(BR), isoprene rubber(IR), styrene–butadiene rubber (SBR), butyl rubber(IIR), halogenated butyl rubber, which is preferably brominated butyl rubber, p-methylstyrene-functionalized butyl rubber (copolymer of isobutylene and p-halomethylstyrene), ethylene–propylene–diene rubber (EPDM), etc.

Natural rubber and the synthetic rubber recited above may be used alone or in combination of two or more according to the rubber article to which the laminate member is applied and the intended extent of reinforcement. A rubber component containing natural rubber and/or a synthetic isoprene rubber in an amount of 50% by weight or more is preferable in view of a sufficient rubber-to-steel cord adhesion and fracture resistance of the vulcanized rubber composition.

The coating rubber composition may further contain an adhesion promoter commonly used in known adhesive rubber compositions for steel cords. The adhesion promoter is, for example, a metal salt of an organic acid, preferably cobalt salt of an organic acid. The organic acid may be either saturated or unsaturated, and either linear or branched. Examples of the organic acid include a naphthenic acid such as cyclohexanecarboxylic acid and an alkylcyclopentane having a fatty acid residue; a saturated fatty acid such as hexanoic acid, octanoic acid, decanoic acid including branched isomers such as neodecanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, and octadecanoic acid; an unsaturated fatty acid such as methacrylic acid, oleic acid,

linoleic acid, and linolenic acid; and resin acid such as rosin, tall oil acid, and abietic acid. Metal element of the metal salt of organic acid may be partly replaced with boron, boric acid, or an aluminum-containing compound. The amount of the metal salt of organic acid to be incorporated, in terms of metal element basis, is 0.1 to 0.3 part by weight based on 100 parts by weight of the rubber component. Also, the adhesion promoter may be incorporated into the rubber composition layer adjoining to the steel cord–coating rubber composite layer.

The rubber composition constituting the tire reinforcing member of the present invention usually contains sulfur preferably in an amount of 3 to 8 parts by weight per 100 parts by weight of the rubber component. When the amount of sulfur is less than 3 parts by weight, the rubber-to-steel cord adhesion may become insufficient because the amount of sulfur for the formation of Cu_xS (formed by the reaction of sulfur and copper in brass-plating layer of steel cords) which contributes to the rubber-to-steel cord adhesion decreases. The use of an amount exceeding 8 parts by weight may cause excessive formation of Cu_xS which may lead to occasional cohesive failure in the thickened Cu_xS, thereby reducing the rubber-to-steel cord adhesion. In addition, the heat aging resistance of the rubber composition tends to be reduced.

In addition to the above additives or components, the coating rubber composition and the rubber composition layer adjoining thereto may further contain another compounding additive commonly used in the rubber art in a usual amount.

Such a compounding additive may includes a filler, a plasticizer, a vulcanization accelerator, and an antioxidant. The filler includes carbon black, zinc white, silica, etc. The plasticizer includes aromatic extract oil. Examples of the vulcanization accelerator include a guanidine compound such as diphenylguanizine, a thiazole compound such as mercaptobenzothiazole, a sulfenamide compound such as N,N'-dicyclohexyl-2-benzothiazolylsulfenamide,

and a thiuram compound such as tetramethylthiuram disulfide. The antioxidant includes an amine compound such as poly(2,2,4-trimethyl-1,2-dihydroquinoline) and phenyl-α-naphthylamine.

To enhance the adhesion to rubber, steel cords used in the reinforcing member of the present invention are preferably metalized with brass or zinc each optionally containing nickel or cobalt by plating. Brass plating is particularly preferable. To obtain a good and stable adhesion, the Cu content in the brass plating is 75% by weight or less, preferably 55 to 70% by weight. The steel cords may be twisted with no specific limitation in the twist structure.

The tire of the present invention is a pneumatic tire to which the tire reinforcing member described above is applied. The tire member to which the tire reinforcing member is applied is not particularly limited, but preferably it is a carcass ply and/or a belt ply. The tire reinforcing member comprises (a) at least one composite layer of steel cords coated with a coating rubber composition and, optionally, (b) at least one rubber composition layer (for example, a so-called squeegee rubber) adjoining to the composite layer. The tire reinforcing member may have a single composite layer, or two or more composite layers. And preferably, the carcass layer has one or two composite layers, and the belt layer has two to six composite layers.

The pneumatic tire of the present invention is preferably used as a truck/bus tire, or a large-sized off-road tire, for example, a tire for construction vehicle such as dump truck, loader, and scraper, in which the resistance to loss of steel cord-to-rubber adhesion is quite important because of a large tire thickness.

The production of the rubber composition, the steel cord-coating rubber composite, the tire reinforcing member and the pneumatic tire described above requires no specific process which needs undue experimentation, and may be accomplished by methods known to one of ordinary skill in the rubber and tire art.

The pneumatic tire of the present invention may be filled with air or with

an inert gas such as nitrogen.

The present invention will be described in further detail by reference to the following examples which are not intended to limit the scope of the present invention thereto.

The initial adhesion and the resistance to adhesion loss of the test tire were evaluated by the following methods.

(1) Initial Adhesion

A sample was cut out from a carcass ply at shoulder portion of a vulcanized tire. Steel cords in the sample were then pulled out at –90°C. The rubber-coated surface area of the pulled-out steel cords was measured, and an amount of remaining-rubber (%) was expressed by the ratio of the rubber-coated surface to the entire surface of the steel cords. The larger the amount of remaining-rubber, the better the initial steel cord-to-rubber adhesion.

(2) Resistance to Adhesion Loss

The vulcanized tire was stored for 15 days at 100°C. Then, the amount of remaining-rubber (%) was determined in the same manner as in (1). The larger the amount of remaining-rubber, the better the resistance to adhesion loss.

EXAMPLES 1–6 and COMPARATIVE EXAMPLES 1–2

An 11R22.5 size truck/bus tire having four belt plies was prepared by a known method. The steel cords (3+9+1 structure with a single cord diameter of 0.23 mm) plated with brass (Cu: 63% by weight, Zn: 37% by weight) were used as the reinforcement for the carcass ply. The carcass ply was made of a tire reinforcing member having one composite layer comprising the steel cords coated with a coating rubber composition and one rubber composition layer (squeegee rubber) adjoining to the composite layer for Examples 1 to 5 and Comparative Example 1 and one composite layer comprising the steel cords coated with a coating rubber composition for Example 6 and Comparative Example 2.

Rubber compositions A to E were used for the coating rubber composition

of the composite layer and the rubber composition of the rubber composition layer in the carcass ply of a test tire. The rubber composition A was prepared by compounding 100 parts by weight of natural rubber, 55 parts by weight of carbon black FEF, 1.0 part by weight of a plasticizer, 2.0 parts by weight of cobalt naphthenate, 6 parts by weight of zinc oxide, 2 parts by weight of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (Nocrac 6C, trade name of Ouchi Shinko Kagaku Kogyo Co., Ltd.) as an antioxidant, 5 parts by weight of sulfur, and 0.8 part by weight of N,N'-dicyclohexyl-2-benzothiazolylsulfenamide (Nocceler DZ, trade name of Ouchi Shinko Kagaku Kogyo Co., Ltd.) as a vulcanization accelerator. The formulation of the rubber composition A was used as a basic formulation. By compounding the basic formulation with a predetermined amount of hydrotalcite (KW-2200, trade mark of Kyowa Chemical Industry Co., Ltd.) or MgO as a basic inorganic filler, as shown in Table 1, each of the rubber composition B to E was prepared.

Table 1

Basic Inorganic Filler (part by weight)	Rubber Compositions A	B	C	D	E
Hydrotalcite	–	0.5	5	10	–
MgO	–	–	–	–	1

The combination of the coating rubber (composite layer) and the squeegee rubber (rubber composition layer) used in the carcass ply of each test tire is shown in Table 2.

Each test tire thus prepared was examined on the initial adhesion and the resistance to adhesion loss in the manner described above. The results are shown in Table 2.

Table 2

	Examples						Comparative Examples	
	1	2	3	4	5	6	1	2
Carcass Ply coating rubber	A	A	A	A	B	B	A	A
squeegee rubber	B	C	D	E	B	none	A	none
Initial adhesion (%)	95	95	95	95	90	90	95	95
Resistance to adhesion loss (%)	40	55	65	45	50	50	10	10

As seen from Table 2, excellent results in both the initial adhesion and the resistance to adhesion loss were obtained in the tires of the present invention with the carcass ply having the hydrotalcite-compounded rubber composition.

The tire reinforcing member of the present invention greatly enhances the resistance to the loss of the steel cord-to-coating rubber adhesion without lowering the initial steel cord-to-coating rubber adhesion. Therefore, the tire reinforcing member provides a pneumatic tire having an dramatically improved endurance.